PATENT

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SPECIFICATION

TO WHOM IT MAY CONCERN

Be it known that I, Kyung-Ju Choi, a citizen of the United States of America and resident of Jefferson County, State of Kentucky, whose Post Office Address is 8406 Running Spring Drive, Louisville, Kentucky, 40241, have invented a certain new and useful method, apparatus and product, namely:

TITLE OF INVENTION	:	METHOD, APPARATUS AND PRODUCT FOR MANUFACTURING NANOFIBER MEDIA
CROSS-REFERENCE TO RELATED APPLICATIONS	:	NOT APPLICABLE
STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT	:	NOT APPLICABLE
SEQUENCE LISTING	:	NOT APPLICABLE

BACKGROUND OF THE INVENTION

The present invention relates to a unified method, apparatus and product arrangement for producing nanofiber filaments and more particularly, to such an arrangement for producing organic filter media nanofibers.

It is well known in fiber manufacture to produce extremely fine fibrous materials of organic fibers, attention being directed to U.S. Patents No. 4,043,331 and No. 4,044,404, issued to G.E. Martin et al on August 23 and August 30, respectively, wherein a fibrillar mat product is prepared by electrostatically spinning an organic material and subsequently collecting spun fibers on a suitable surface; No. 4,266,918, issued to R.S. Manley on May 12, 1981, wherein a controlled pressure is applied to a molten polymer which is emitted through an orifice of an energy charged plate; and, to No. 4,323,525, issued to A. Bornat on April 6, 1982, wherein a water soluble polymer is fed by a series of spaced syringes into an electric field including an energy charged metal mandrel having a sheath of aluminum foil wrapper therearound which may be coated with PTFE (Teflon^{TM}) release agent. Attention is further directed to U.S. Patents No. 4,044,404, issued to G. Ernest on August 30, 1977, No. 4,639,390, issued to R. Shoji on Jan. 27, 1987; No. 4,657,743, issued to A.C. Fisher on April 14, 1987; No. 4,842,505, issued to D. Annis et al on June 27, 1989; No. 5,522,879, issued to A.G. Scopelianos on June 4, 1996, No. 6,106,913, issued to F. L. Scardino et al on August 22, 2000; and, No. 6,111,590, issued to S. Zarkoob et al on August 29, 2000 – all of which use polymer nanofiber production arrangements. Finally, attention is directed to the nanofiber polymer spinning article entitled, "Development of Non-wovens for Protective Clothing: "Nanofiber Membrane Example", by P. Gibson et al, published on 9th Annual TANDEC Nonwovens Conference, November 10-12, 1999 by the U.S. Army Soldier Systems Center, Natick MA.

In all of the above prior art, none – either alone or in combination – recognizes let alone teaches, the novel, unified electro-spinning method, apparatus and product arrangement hereinafter set forth. In accordance with the present invention, it is recognized that solvent recovery is a most critical issue, since solvents for most polymers are organic and harmful. Moreover, the fiber tensile strength has proven to be very low with the produced fibers dissolving in water, including environmentally humid conditions. The continuous, uninterrupted manufacturing process of elecrospinning is an important feature of the present invention. A further feature of the present invention is to provide for uniform coverage across a full width of a product through the novel usage of multiple capillary tubes. To further increase production output, the present invention recognizes the advantages of manufacturing tubular capillary tubes with sharp plural outlet tips and with the application of heat surrounding the capillary tubes to further improve output. The present invention, recognizing these past problems in the electro-spinning of water soluble polymeric material, provides a unique arrangement wherein nanofibers can be significantly reduced to very thin cross-sectional areas and yet be produced under unique alternative pressure steps, resulting in a comparatively stronger and more flexible nanofibers. The nanofibers produced by the unique electro-spinning arrangement of the present invention allow for a safe environment with the produced nanofibers being comparatively stronger and having good adhesion and flexibility when mounted to a substrate, allowing for a minimum increase of pressure drop across the manufactured product. In addition, products produced by the unique electro-spinning arrangement of the present invention maintain a comparatively high porous integrity with such lower pressure drop, resulting in higher product efficiency – particularly of significance in the environmental fluid filtration arts. The unique properties of fibers are arrived at in the present invention by combining selected greater portions by weight of

water soluble polymers with a selected lesser portion by weight of cross-linkable agent capable of forming three dimensional structural unit molecules with the balance by weight being water. In accordance with the present invention, a selected acid can be added to increase the rate of chemical cross-linking. In addition, heat or ultra violet (UV) light can be applied to enhance cross-linking reaction as the nanofibers are formed. In some selected instances the novel nanofibers can be collected on an acid-water soaked substrate.

Various other features of the present invention will become obvious to one skilled in the art upon reading the disclosure set forth herein.

BRIEF SUMMARY OF THE INVENTION

More particularly, the present invention provides a unique and novel unified arrangement which includes: a method of forming nanofibrous media strands comprising: chemically combining a greater portion by weight of a water-soluble polymer with a lesser portion by weight of a cross-linking chemical agent into a chemical combination capable of preventing the polymer of said water-soluble polymer from dissolving in water, including an ambient humid environment; spinning the chemical combination at selected high energy to form very thin spun nanofiber strands of sufficient strength and flexibility to permit product shaping; and, collecting the spun strands on a selected substrate. In selected instances, a lesser portion by weight of an acid can be added to increase the rate of chemical cross-linking. Further, heat of ultraviolet light can be applied to enhance cross-linking reaction as the nanofiber strands are formed.

In addition, the present invention provides a unique apparatus for forming such nanofibrous media comprising: storage means to receive the fiber forming chemical compound including at least one storage inlet to receive the nanofiber forming compound and at least one

valved outlet; pumping means having at least one pumping inlet communicably connected to the valved outlet of the storage means to receive the nanofiber forming compound, the pumping means having at least one pump inlet and at least one pump outlet from which the nanofiber forming compound received by the pumping means can be pumped as at least one stream under selected pressure; energy conductive capillary means having at least one inlet to receive the nanofiber forming compound stream from the pumping means and at least one outlet to emit the nanofiber stream as a thin further reduced fiber stream of selected cross-sectional area with energy generating means connected to the energy conductive capillary means to apply a selected energy charge to the capillary means; insulating means positioned between said pumping means and the capillary means to insulate the fiber stream as it passes from the pumping means to the capillary means; and, collecting means to receive the nanofibers from the capillary means.

Finally, the present invention provides a unique and unified nanofiber media compound arrangement comprised of a greater portion by weight of a water-soluble polymer and a lesser portion by weight of a cross-linking chemical agent with the balance by weight being water, the combination being selected to prevent the polymer of the water-soluble polymer from dissolving in water, including an ambient humid environment. If elected, a lesser portion by weight of an acid may be added to the compound to increase rate of cross-linking. Further, heat and/or ultraviolet light may be applied to enhance cross-linking reaction as the nanofibers are formed. Moreover, the nanofibers may be collected on an acid-water soaked substrate.

It is to be understood that various changes can be made by one skilled in the art in one or more of the several steps, parts and materials described herein without departing from the scope or spirit of the present inventive method, apparatus and product, respectively described herein.

DETAILED DESCRIPTION OF THE DRAWINGS

Referring to the drawings which disclose several advantageous embodiments of the present invention:

Figure 1 is a vertically extending schematic plan view of one unique and novel arrangement of apparatus which may be employed to carry out the present invention;

Figure 2 is a vertically extending schematic plan view, similar to the view of Figure 1 of another unique and novel arrangement which may be employed to carry out present invention;

Figures 3A, 3B and 3C disclose somewhat enlarged views of three types of novel capillary tube tips which may be employed to increase output; and,

Figure 4 discloses a heating arrangement for the capillary tube of Figure 3B.

DETAILED DESCRIPTION OF THE INVENTION

In Figure 1 of the drawing, there is disclosed a longitudinally extending , vertical storage tank 2 which can have a selected capacity in accordance with the novel product to be manufactured. Storage tank 2 which can be formed from any one of a number of suitable liquid impervious materials, such as polyethylene or nylon, can be of cylindrical shape to extend with its longitudinal axis in a supported, substantially vertical position. Storage tank 2 includes a material inlet 3 at the upper portion thereof and, a downwarly necking truncated lower portion 4, having a valved outlet 6 of selected internal cross-section capable of emitting a fluid stream therefrom at a selected volumetric rate. Typically, storage tank 2 can have an internal capacity in the approximate range of fifty (50) to twenty thousand (20,000) cubic centimeters and advantageously two thousand (2,000) cubic centimeters. In Figures 1 and 2, where four (4) capillary tubes are utilized, valved outlet 6 can be controlled to emit a fluid stream in the

approximate range of zero point zero two four (0.024) to eighty (80) cubic centimeters per minute and advantageously two point four (2.4) cubic centimeters per minute. The viscosity of such fluid stream desirably can be in the approximate range of as low as one (1) to one hundred thousand (100,000) poise and advantageously at approximately two hundred eighty (280) poise. A longitudinally extending, vertical pressure leveling tank 5, similar to tank 2 is positioned therebelow. Tank 5 includes a level switch 10 which is connected to valve outlet 6'. This arrangement controls the amount of material fed from storage tank 4 to leveling tank 5 and thus the material pressure therebelow. A suitable control valve 6' is positioned below leveling tank 5.

A plurality of spaced suitable plastic tubings 7 are each connected at one end to valved outlet 6' of pressure leveling tank 5 and at the opposite end to one of a set of several spaced pumps 8 positioned below valved outlet 6'. In an alternative embodiment of the present invention (Figure 2), pumps 8 electively can be eliminated, depending on control of leveling tank 5 to maintain a preselected material pressure.

In accordance with the present invention (Figure 1), each pump 8 can be of a gear type, serving to further stir and reduce the material received thereby and to further reduce the fluid stream emitted therefrom. In the present invention, each fluid stream emitted therefrom can be in the approximate range of zero point zero zero eight (0.008) to twenty point zero (20.0) cubic centimeters per minute and advantageously zero point six (0.6) cubic centimeters per minute with the emitted fluid pressure of the stream being slightly higher than atmospheric pressure. A set of suitable vertically extending electrical insulating tubings 9 are provided to surround each of the fluid streams which are emitted from gear pumps 8. These insulating tubings 9, which can be of energy insulating plastic, are arranged to extend through a horizontally extending sheet 11 of electrically insulating material such as polytetrafluro eythylene (PTFE – Teflon™). The

lower end of each tubing 9 (Figure 3A) surrounds the upper portion of each of a set of spaced electrically conductive capillary tubes 12', each capillary tube 12' having at least (Figure 3A) one sharp tapered tip 13 (Figure 1 and 2 each showing two tips 13') being formed from any one of a number of suitable electrically conductive materials such as copper, silver or stainless steel. Each capillary tube 12' with sharp tapered tips 13' is provided with an upper inlet to receive one of the fluid streams emitted from each of spaced gear pumps 8. The inner diameter of the lower outlet of each capillary tube 12' is internally sized in the approximate range of zero point one (0.1) to three (3) millimeters. As can be seen in Figures 3B and 3C, the capillary tubes 12' and 12" are shown as provided with two tips 13' and four tips 13", respectively, with the diameter of each tip being in the approximate range of zero point one (0.1) to three (3) millimeters. Each electrically conductive capillary tube 12' with sharp tapered tips 13' of Figure 1 is electrically connected to a high voltage electrical generator 16 capable of applying high voltages to each capillary tube with sharp tapered tip 13' in the approximate range of three (3) to one hundred (100) kilovolts and advantageously approximately fifteen (15) kilovolts. Further, and as can be seen in Figure 4, an electrical heating coil 20 can be provided to surround tube 12' so as to warm tube 12' to approximately sixty (60) degrees centigrade (^{o}C) to reduce the surface tension.

Suitably positioned below the spaced set of capillary tubes 12' with sharp tapered tip, 13' to receive the very fine spaced nanofibers emitted therefrom being in the approximate range of zero point one (0.1) to three (3) millimeters is a motor driven, grounded cylindrical drum 17. Drum 17, which can be formed from any one of a number of suitable materials such as copper or stainless steel, can be provided with a suitable porous mat 18 of suitable materials such as porous paper or fiberglass in sheet form which can be movably passed thereover to receive the nanofiber webs from the set of capillary tubes 12' with sharp tapered tips 13'. It is to be understood that

the core of drum 17 can be oppositely charged from generator 16 by a suitable generator 25 if so desired.

It is further to be understood that the inventive arrangement of the aforedescribed storage tank, pump set, capillary tubes with sharp tapered tip or tips and collector structure can be varied in structural form, size and pressures by one skilled in the art without departing from the novel scope of the present unique arrangement described herein above. In this regard and as can be seen in Figure 2 of the drawings, and as aforenoted, in another embodiment of the present invention, gear pumps 8 can be eliminated, with the material pressure being controlled entirely by leveling tank 5 and leveling switch 10.

With the inventive arrangement of apparatus as above-described, the unique and novel method of producing a nanofiber strand product, such as filter media suitable for fluid filtration can include chemically compounding a compound of a greater portion by weight of approximately three (3) to fifty (50) percent of a water-soluble polymer such as polyvinyl alcohol with a lesser portion by weight of a cross-linking chemical agent of approximately zero point one (0.1) to twenty (20) percent and advantageously two (2) percent by weight in water with the balance by weight being pure or acidic water. The cross-linking chemical agent advantageously forms three dimensional submicroscopic structural molecules which prevent the polymer of the greater portion of the water-soluble polymer from dissolving in water, including ambient humid environment. Advantageously, the lesser portion by weight of a cross-linking chemical agent can be a selected chemical such as one of the di-aldehydes; namely, Glyoxal ($C_2H_2O_2$), Glutaraldehyde ($C_5H_8O_2$) or one of the acids; namely Maleic acid ($C_4H_4O_4$) or Borax ($B_4N_{a2}O_2$). Further, a selected acid, such as phosphoric acid, can be added in order to increase the rate of cross-linking process. Heat or ultra violet (UV) light can be applied to enhance cross-

linking reaction as the nanofibers are formed. In some instances, the nanofibers can be collected on an acid-water soaked substrate.

With selected quantities of either of such chemical combinations in a storage zone, such as storage tank 2, selected quantities thereof can then be passed to a pumping zone; the pumping zone disclosed including, (Figure 1) or not including (Figure 2),the set of spaced gear pumps 8. From the pumping zone, selected quantities of the chemical compound can be passed through suitable plastic tubing 7 surrounded by insulating material such as insulating tubes 9 through a porous electrically insulated zone, hereabove described as PTFE sheet 11. The fluid streams are passed into a capillary tube feeding zone in the form of spaced capillary tubes 12' with sharp tapered tips 13'. Capillary tubes 12' are charged by high voltage generation in the approximate voltage range of three (3) to one hundred (100) kilovolts and advantageously fifteen (15) kilovolts. In the present invention, each fluid stream emitted from a capillary tube 12' can be in the approximate range of zero point zero zero eight (0.008) to twenty (20) cubic centimeters per minute and advantageously zero point six (0.6) cubic centimeters per minute with the emitted fluid pressure of the stream being slightly higher than atmospheric pressure. The nanofiber filter threads are collected on a filter media collector zone substrate such as a selected porous sheet of paper or porous fiberglass sheet 18 movably mounted on motor driven collector drum 17.

The inventive formed nano fiber media comprises chemically compounding a compound of a greater portion by weight of approximately three (3) to fifty (50) percent of water-soluble polymer such as polyvinyl alcohol with a lesser portion by weight of a cross-linking chemical agent of approximately zero point one (0.1) to twenty (20) percent and advantageously two (2) percent by weight in water with the balance by weight being pure or acidic water. The cross-linking chemical agent advantageously forms three dimensional submicroscopic structural

molecules which prevents the polymer of the greater portion of the water-soluble polymer from dissolving in water, including an ambient humid environment. Advantageously, as above described, the lesser portion by weight of a cross-linking chemical agent can be a selected chemical such as di-aldehydes; namely Glyoxal ($C_2H_2O_2$) or Glutaraldehyde ($C_5H_8O_2$) or acids; namely Maleic acid ($C_4H_4O_4$) or Borax ($B_4N_{a2}O_2$). A selected acid, such as phosphoric acid, can be added in order to increase the rate of cross-linking process. Heat or ultra violet (UV) light can be applied to enhance cross-linking reaction as the nanofibers are formed. In some case, these nanofibers can be collected on an acid-water soaked substrate.

The size of the nanofibers advantageously can have a range from thirty (30) to one thousand (1,000) nanometers and advantageously one hundred fifty (150) nanometers formed as a filter mat by itself or with a porous filter substrate of either another fiber, which also can be of a different nano fibers – or a porous paper, each of selected thickness.

The invention claimed is: